

JAPANESE

[JP,2000-345029,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT  
OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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**DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Reinforced polyamide resin (A) which was distributed uniformly | the silicate layers of a sheet silicate | at a molecular level as for this invention 99 to 50 % of the weight, and liquid crystal polymer (B) It consists of 1 to 50 % of the weight, and it is lightweight, excels in heat resistance or rigidity, and is related with the polyamide system composite material which can be suitably used as a damping nature injection-molded product.

[0002]

[Description of the Prior Art]Since it has mechanical properties excellent in the mold goods, polyamide resin is especially used broadly as an injection molding material for parts, such as a car and home electronics. When making high rigidity and heat resistance give polyamide mold goods, the polyamide resin composition usually strengthened with the fibrous reinforcing material is used.

For example, the polyamide resin composition which carried out specific amount combination of the glass fiber as a fibrous reinforcing material is proposed (JP,51-50960,A, the 54 No. -18854 gazette, a 59-168058 gazette).

However, since the mold goods using the aforementioned polyamide resin composition have small internal loss (tan delta), damping performances have deficiently a problem that dimensional accuracy is low. There is also a problem that it is difficult to obtain lightweight mold goods.

[0003]Improving the dimensional accuracy of mold goods and rigidity is proposed by adding powdered inorganic substances, such as glass fiber and talc, to polyamide resin (JP,58-4737,B, JP,51-7056,A). However, in a polyamide resin composition given in here, the addition of glass fiber is | the addition of an inorganic substance | 20 % of the weight or more at 15 or less % of the weight, and since | with few fibrous reinforcing materials | there are many inorganic substances, there is a problem that a specific Young's modulus (the rate of bending flexibility / specific gravity) required as a high-damping material does not become large.

[0004]The low camber nature polyamide resin composition which consists of reinforced polyamide resin in which montmorillonite was uniformly distributed with the molecular level on the other hand, and a fibrous reinforcing material is proposed (the \*\*\*\*\* No. 2528164 gazette). However, when there are many loadings of glass fiber also in this case, the improvement effect of a weight saving or a specific Young's modulus is not enough.

[0005]

[Problem(s) to be Solved by the Invention]The polyamide system composite material which is lightweight as for this invention, and is excellent in heat resistance or rigidity, and can be suitably used as a damping nature injection-molded product, and the injection-molded product which used this for the row are provided.

[0006]

[Means for Solving the Problem]Then, as a result of repeating examination wholeheartedly, this invention persons found out that an aforementioned problem was solvable by carrying out specific amount combination of the liquid crystal polymer to reinforced polyamide resin in which silicate layers of a sheet silicate were uniformly distributed with a molecular level, and reached it at this invention.

[0007]That is, the gist of this invention is as follows.

(1) Reinforced polyamide resin (A) in which silicate layers of a sheet silicate were uniformly distributed with a molecular level 99 to 50 % of the weight, and liquid crystal polymer (B) Polyamide system composite material which consists of 1 to 50 % of the weight.

(2) Specific gravity. Polyamide system composite material of the above-mentioned (1) statement whose specific Young's modulus (the rate of bending flexibility / specific gravity) is 5 or more GPa or less in 1.3.

(3) Above (1) Or (2) Injection-molded product using a polyamide system composite material of a statement.

[0008]

[Embodiment of the Invention]Hereafter, this invention is explained in detail. 99 to 50 % of the weight of reinforced polyamide resin (A) and the liquid crystal polymer (B) by which the silicate layers of the sheet silicate were uniformly distributed with the molecular level as for the polyamide system composite material of this invention It is required to consist of 1 to 50 % of the weight, Specific gravity. It is preferred that a specific Young's modulus (the rate of bending flexibility / specific gravity) is 5 or more GPa at 1.3 or less. Liquid crystal polymer (B) At less than 1 % of the weight, the improved effect of a specific Young's modulus is not revealed for a blending ratio. On the other hand, if this \*\*\*\*\* exceeds 50 % of the weight, since pelletizing by melt kneading extrusion will become difficult and shock resistance will also fall further, it is not desirable.

[0009]Reinforced polyamide resin (A) in this invention The silicate layers of a sheet silicate are uniformly distributed with a molecular level in polyamide resin. Silicate layers are basic units which constitute a sheet silicate here, and it is obtained by carrying out cleavage of the sheet silicate. When a sheet silicate distributes distributing with a molecular level in polyamide resin, the state where each is maintained at not less than an average of 20A interlaminar distance is said, moreover -- interlaminar distance meaning the distance between the monotonous center of gravity of said silicate layers, and distributing uniformly -- every sheet of silicate layers -- or the multilayer thing of five or less layers is in the state in which parallel and random were intermingled at random in parallel, and an average lap. The state of distributing without the not less than 50% being [ not less than 70% of ] preferred, and forming a lump is said. Specifically, it is reinforced polyamide resin (A). Wide angle X diffraction measurement is performed about a pellet, and it can check from the peak resulting from the thickness direction of silicate layers having disappeared.

[0010]Reinforced polyamide resin (A) The polyamide resin to constitute is a polymer which has an amide bond formed from amino acid, lactam or diamine, and dicarboxylic

acid (the salt of the couple of them is also contained.). As a desirable example of such polyamide resin, PORIKA pro amide (nylon 6), polytetra ethylene adipamide (Nylon 46), Polyhexamethylene adipamide (Nylon 66), polyhexamethylene sebacamide (nylon 610), Polyhexamethylene DODEKAMIDO (nylon 612), polyundecamethylene adipamide (nylon 116), Poly UNDEKAMIDO (Nylon 11), poly DODEKAMIDO (Nylon 12), Polytrimethyl hexamethylphthalamide (nylon TMDT), Polyhexamethylenisophthalamide (nylon 6 I), polyhexamethylene terephthal / isophthalamide (nylon 6 T/6I), Polybis(4-aminocyclohexyl)methane DODEKAMIDO (nylon PACM12), Polybis(3-methyl-4-aminocyclohexyl)methane DODEKAMIDO (nylon dimethyl PACM12), Polymetaxylylene adipamide (Nylon MXD 6), poly nonamethyleneterephthalamido (nylon 9T), polyundecamethylene terephthalamide (nylon 11T), polyundecamethylene hexahydro terephthalamide [Nylon 11 T (H)] Or such copolymerization polyamide, mixed polyamide, etc. are mentioned, also in it, nylon 6 or such copolymerization polyamide, Nylon 66, or such copolymerization polyamide are preferred, and nylon 6 and especially Nylon 66 are preferred.

[0011]With the value calculated on with the temperature of 25 \*\*, and a concentration of 1 g/dl conditions using 96-% of the weight concentrated sulfuric acid as a solvent although the relative viscosity in particular of polyamide resin is not limited It is preferred that it is in the range of 1.5-5.0, and especially the thing of the range of 2.0-3.5 is preferred. This relative viscosity. In less than 1.5 thing, a mechanical property when it is considered as mold goods falls. On the other hand, this relative viscosity In the thing exceeding 5.0, a moldability falls remarkably.

[0012]Reinforced polyamide resin (A) As a sheet silicate to constitute, a smectite group (for example, montmorillonite, a BANDE light, and saponite.) Hectorite, a saconite, a vermiculite group (for example, vermiculite), a mica group (for example, fluoride mica, white mica, palagonite phlogopite, and black mica.) Although hydrous inosilicate system minerals, such as a REPIDO night, a brittle mica group (for example, margarite, a klint night, Annan Daito), a chlorite group (for example, a DOMBA site, SUDOAITO, KUKKEAITO, KURINOKUROA, a game fowl night, Nima Ito), and sepiolite, etc. are mentioned. In these, a swelling fluoride mica system mineral (what replaced the hydroxyl group of mica with fluoride, and henceforth "fluoride mica") is preferred in respect of the dispersibility of the silicate layers in polyamide resin.

[0013]Said fluoride mica is shown by the following formula and can be compounded easily.

$\alpha\text{MgF}_2$  and  $\beta\text{MgF}_2$  and  $\gamma\text{SiO}_2$  (among a formula) M expresses sodium or lithium, and  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $a$ , and  $b$  express calculation respectively, and are  $0.1 \leq \alpha \leq 2$ ,  $2 \leq \beta \leq 3.5$ ,  $3 \leq \gamma \leq 4$ ,  $0 \leq a \leq 1$ ,  $0 \leq b \leq 1$ , and  $a + b = 1$ .

[0014]There is what is called scorification that mixes oxidized silicon, magnesium oxide, and various kinds of fluorides as a manufacturing method of such fluoride mica, fuses the mixture thoroughly at the temperature of 1400-1500 \*\* with an electric furnace or a gas furnace, and carries out crystal growth of the fluoride mica into a reaction vessel by the cooling process. There is a method of carrying out the intercalation of the alkali metal ion to this, and obtaining fluoride mica, using talc as a starting material (JP,2-149415,A). In this method, \*\* fluoride alkali or fluoridation alkali is mixed to talc, and it is within a porcelain crucible. Fluoride mica can be obtained by carrying out short-time heat-treatment at 700-1200 \*\*.

[0015]Reinforced polyamide resin (A) What is necessary is just to polymerize monomers, such as the aminocaproic acid, lactam or diamine which forms polyamide resin, and dicarboxylic acid, under existence of the sheet silicate of the specified quantity, in order to obtain. It can also obtain by carrying out melt kneading of the sheet silicate and polyamide resin which were beforehand pretreated with onium salt.

[0016]Under the present circumstances, in order to consider it as the injection-molded product which is mixed with the liquid crystal polymer mentioned later as loadings of a

sheet silicate, is lightweight, and is excellent in heat resistance or rigidity, and has damping nature. The monomer amount which forms polyamide resin 100 weight section, or polyamide resin It is preferred to consider it as one to 10 weight section to 100 weight sections. These loadings can reveal neither heat resistance nor a rigid improved effect easily in less than one weight section. On the other hand, if these loadings exceed ten weight sections, it becomes difficult, and toughness will also fall and the weight saving of mold goods will become weak.

[0017]reinforced polyamide resin (A) \*\*\*\* -- paints, a release agent, a thermostabilizer, an antioxidant, fire retardant, a plasticizer, etc. can be added in the range which does not spoil the characteristic greatly. These are the time of a polymerization, or the obtained reinforced polyamide resin (A). It is added when carrying out melt kneading.

[0018]Liquid crystal polymer (B) in this invention There is molecule combination by a molten state and anisotropy is shown optically. As a desirable example of such a liquid crystal polymer, \*\* The copolymerized polyester which consists of the ethylene terephthalate unit and Para hydroxybenzoic acid residue unit which were indicated by JP,50-18016,B, \*\* The copolymerized polyester which consists of the 6-hydroxy-2-naphthoic acid residue unit and Para hydroxybenzoic acid residue unit which were indicated by JP,54-77691,B, \*\* The Para hydroxybenzoic acid residue unit indicated by JP,47-47870,B, The copolymerized polyester which consists of a terephthal acid residue unit and a bisphenol residue unit, \*\* The copolymerized polyester which consists of a terephthal acid residue unit indicated by JP,53-65421,B and a phenylhydroquinone residue unit, \*\* Although the copolymerized polyester etc. which consist of the terephthal acid residue unit, phenylhydroquinone residue unit, and SUCHIRO yl hydroquinone residue unit which were indicated by the U.S. Pat. No. 4,600,765 specification are mentioned, copolymerized polyester of \*\* is preferred in respect of a moldability.

[0019]Although the logarithmic viscosity in particular of a liquid crystal polymer is not limited, pentafluoro phenol is used for it as a solvent, and it is the temperature of 60 \*\*, and concentration. It is preferred that it is in the range of 2-10 with the value calculated on 0.1-g/dl conditions. A mechanical property when this logarithmic viscosity considers it as mold goods in less than two thing falls. On the other hand, in that in which this logarithmic viscosity exceeds 10, a moldability falls remarkably.

[0020]In order to manufacture the polyamide system composite material of this invention, Usually, the above-mentioned reinforced polyamide resin (A) A pellet and liquid crystal polymer (B) A pellet, What is necessary is to carry out melt kneading using the biaxial extrusion machine provided with the screw, to extrude to strand shape, and just to pelletize, after carrying out a dry blend uniformly using a tumbler or a Henschel mixer. And it is considered as various kinds of mold goods by injection molding using the pellet of the obtained composite material.

[0021]The mold goods obtained using the polyamide system composite material of this invention are notably improved compared with the case where mechanical performances, such as flexural rigidity and flexural strength, heat resistance, dimensional accuracy, damping performances, etc. are polyamide resin independent, and since there are few mechanical properties and the dimensional changes by water absorption, they can be used as various kinds of mold goods.

[0022]as the above-mentioned mold goods, there are AV parts, such as structural parts, such as room mirrors, such as a body part of the circumference of the engine of cars, such as a gearbox, and a door mirror stay, and a fender mirror, and a digital disk, parts for speakers, etc. as a field as which damping performances are required, for example. As a field as which heat resistance and dimensional accuracy are required, electronic parts, such as breaker covering, a switch, and a connector, etc. can be mentioned. However, it can use for the field which can employ efficiently not the thing limited to these but the light weight which is the characteristic of the polyamide system composite material of this invention and the outstanding heat resistance, and rigidity

broadly.

[0023]

[Example]Next, an example explains this invention still more concretely. The measuring method of the raw material used by the example and the comparative example and a physical-properties examination is as follows.

1. Raw material (1) As opposed to the talc ground so that mean particle diameter might be set to 4 micrometers with a fluoride mica ball mill, Mean particle diameter mixes the \*\* sodium fluoride which is similarly 4 micrometers so that it may become 15% of the weight of the whole quantity, this is put into a porcelain crucible, and it is an electric furnace. It heat-treated at 850 \*\* for 1 hour, and fluoride mica was compounded. As a result of performing wide angle X diffraction measurement (the Rigaku make and RAD-B type X-ray diffractometer are used) about the powder of this fluoride mica, it is the thickness of c shaft orientations of raw material talc. The peak over 9.2 Å disappeared and the peak corresponding to 12-13 Å which shows generation of fluoride mica was accepted.

(2) After carrying out swelling processing of the montmorillonite (the Kunimine Industries make, KUNIPIAF) of montmorillonite marketing by the hydrochloride of 12-amino dodecanoic acid underwater, the thing which was dried [ which dried, and filtered and was rinsed ] and ground was used. It was checked that the thickness of c shaft orientations of montmorillonite increases from 12 Å to 17 Å, and 12-amino dodecanoic acid is inserted between the layers of montmorillonite about this powder as a result of performing wide angle X diffraction measurement.

(3) Reinforced polyamide resin (A-1)

To 10 kg of epsilon caprolactam, 1 kg of water and 400 g of fluoride mica are added, this is put into autoclave with a content volume of 30 l., and it heats to 260 \*\*, and it was made to go up until internal pressure became 15kg/cm<sup>2</sup> ]. They are pressure 15 kg/cm<sup>2</sup> and temperature, emitting a steam gradually after that. After polymerizing for 2 hours, holding at 260 \*\*, pressure was discharged to ordinary pressure over 1 hour, and it polymerized for 40 more minutes. When the polymerization was completed, the above-mentioned resultant was paid out to strand shape, after cooling and solidification, it cut and the pellet of reinforced polyamide resin was obtained. Subsequently, after 95 \*\* hot water performed scouring for 8 hours, vacuum drying of this pellet was carried out. The obtained reinforced polyamide resin is silicate layers. It contained 4.4% of the weight, and relative viscosity was 2.5. When wide angle X diffraction measurement was performed about the pellet of this reinforced polyamide resin, it turned out that the peak of the thickness direction of fluoride mica has disappeared thoroughly, and fluoride mica is uniformly distributed in polyamide resin.

(4) Reinforced polyamide resin (A-2)

450 g of montmorillonite was used instead of 400 g of fluoride mica, and also it is (3). Reinforced polyamide resin was obtained like the shown method. The obtained reinforced polyamide resin is silicate layers. It contained 5.0% of the weight, and relative viscosity was 2.5. When wide angle X diffraction measurement was performed about the pellet of this reinforced polyamide resin, it turned out that the peak of the thickness direction of montmorillonite has disappeared thoroughly and montmorillonite is uniformly distributed in polyamide resin.

(5) Glass fiber reinforced nylon 6 (N6G)

The Unitika, Ltd. make and A1030GFL (6) Minerals restoration nylon 6 (N6l)

The Unitika, Ltd. make and A3130 (7) Liquid crystal polymer (LCP)

The Unitika, Ltd. make, rod run LC-5000 [0024]2. Measuring method (a) Based on specific gravity ASTM D792, it asked with the underwater substitution method.

(b) It asked based on rate ASTM Dof bending flexibility790.

(c) It defines as the rate of specific-Young's-modulus bending flexibility / specific gravity.

(d) Based on load deflection temperature ASTM D648, it asked by load 1.8MPa.

## (e) Internal loss (tandelta)

ASTM D790 The specimen (for bending tests) was cut and it was considered as the 225mm x 12.5mm x 3.0mm (length x width x thickness) specimen. Next, tandelta at 20 \*\* was measured by the exciting method using a servo analyzer (the product made by ADVANTEST, R92CFTT). Damping performances are excellent, so that tandelta is large.

[0025]It is resin temperature with the twin screw extruder (the Ikegai Corp. make, PCM-30) after carrying out the dry blend of Example 1 - 3 reinforced polyamide resin (A-1), and the liquid crystal polymer (LCP) by the blending ratio (% of the weight) shown in Table 1. At 290 \*\*, it melt-kneading-extruded and pelletized. Subsequently, an injection molding machine (the Toshiba Machine Co., Ltd. make, IS100E-3A) is used after drying this pellet, and it is a cylinder temperature, 300 \*\*, die temperature. The predetermined ASTM examination was produced by carrying out injection molding on 100 \*\* conditions. After allowing these specimens to stand at a room temperature on the 1st, specific gravity, the rate of bending flexibility, load deflection temperature, and tandelta were measured.

[0026]A-2 was used instead of Example 4 - 6A-1, and also the ASTM specimen was produced like Examples 1-3, and the physical-properties examination was presented, respectively.

[0027]The result in Examples 1-6 is collectively shown in Table 1.

[0028]

[Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6
配合割合	強化剤/樹脂	A - 1 (wt%)	90	70	50	—	—
		A - 2 (wt%)	—	—	—	90	70
	液晶ポリマー	L C P (wt%)	10	30	50	10	30
試験片 の 物性	比重	(—)	1.18	1.23	1.28	1.18	1.23
	曲げ弾性率	(GPa)	5.9	6.8	7.6	5.9	6.8
	比弾性率	(GPa)	5.0	5.5	5.9	5.0	5.5
	荷重たわみ温度	(℃)	157	160	163	157	160
	tan δ	(—)	0.025	0.033	0.042	0.025	0.033

[0029]N6G (comparative example 1) or N6I (comparative example 2) was used instead of comparative example 1 and 2A-1, and also the ASTM specimen was produced like Example 2, and the physical-properties examination was presented, respectively.

[0030]An injection molding machine (the Toshiba Machine Co., Ltd. make, IS100E-3A) is used after drying the pellet of comparative example 3 reinforced polyamide resin (A-1), and it is a cylinder temperature. The predetermined ASTM specimen was produced by carrying out injection molding on 260 \*\* and conditions with a die temperature of 70 \*\*. After allowing these specimens to stand at a room temperature on the 1st, specific gravity, the rate of bending flexibility, load deflection temperature, and tandelta were measured.

[0031]A-2 was used instead of comparative example 4A-1, and also the ASTM specimen was produced like the comparative example 3, and the physical-properties examination was presented, respectively.

[0032]The result in the comparative examples 1-4 is collectively shown in Table 2.

[0033]

[Table 2]

			比較例 1	比較例 2	比較例 3	比較例 4
配合割合	強化剤として樹脂	A-1 (wt%)	—	—	100	—
		A-2 (wt%)	—	—	—	100
		N 6 G (wt%)	70	—	—	—
		N 6 I (wt%)	—	70	—	—
	液晶ポリマー	L C P (wt%)	30	30	—	—
試験片の物性	比重	(—)	1.38	1.42	1.15	1.15
	曲げ弾性率	(GPa)	7.8	7.0	5.5	5.4
	比弾性率	(GPa)	5.7	4.9	4.8	4.7
	荷重たわみ温度	(℃)	190	168	156	155
	$\tan \delta$	(—)	0.030	0.030	0.020	0.020

[0034]  
 [Effect of the Invention] According to this invention, it is lightweight, and excels in heat resistance or rigidity, and the polyamide system composite material which can be suitably used as a damping nature injection-molded product can be obtained.

[Translation done.]